

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Purification of Phenol

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

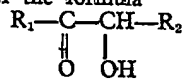
The present invention relates to the purification of phenols and in particular to the purification of phenol derived from cumene.

The production of phenol by the oxidation of cumene and the decomposition of the resulting hydroperoxide is well known. The phenol produced in this process can be purified by conventional methods to a degree which satisfies the exacting requirements of the British Standard Specification and of the U.S. Pharmacopeia. However, some samples of highly purified phenol produced in this way, while conforming to these specifications, still contain impurities which cause the development of an undesired colour when the phenol is subjected to chlorination, particularly to the mono- and penta-chlor-phenols, or on sulphonation with concentrated sulphuric acid. These impurities are referred to in this specification as "colour forming impurities".

According to the present invention the process for the purification of phenol derived from cumene and containing colour forming impurities including aliphatic α -hydroxy carbonyl compounds comprises subjecting the impure phenol at an elevated temperature to conditions which will cause the substantially complete condensation of the aliphatic α -hydroxy carbonyl compounds with phenol to form benzofurans, and separating the phenol substantially completely from the benzofurans.

The invention is based on the discovery that the undesired colour which develops when the phenol is subjected to chlorination and/or

sulphonation is at least partially due to the presence in the phenol of very small quantities of one or more benzofurans, which, under chlorination and/or sulphonation conditions react to give intensely coloured derivatives. It has further been discovered that these benzofurans are formed by the condensation of phenol with various precursors including aliphatic α -hydroxy carbonyl compounds, i.e. compounds of the formula



R_1 and R_2 being hydrogen atoms or alkyl groups. Such compounds include hydroxyacetone (acetol) and acetyl methyl carbinol (acetoin). Thus it is believed that hydroxyacetone condenses with phenol to form 2-methyl-benzofuran, while acetoin condenses with phenol to form 2,3-dimethylbenzofuran. Chlorination and/or sulphonation colour can also be caused by the presence in the phenol of condensation products other than benzofurans, which are derived from various precursors including aliphatic α -hydroxy carbonyl compounds, such as hydroxyacetone and acetoin, as well as compounds such as diacetyl and mesityl oxide. It has been found that the conditions which will cause the conversion of aliphatic α -hydroxy carbonyl compounds to substituted benzofurans also result in the formation of these other colour-forming condensation products, and in the conversion of the aliphatic α -hydroxy carbonyl compounds in part to impurities which are not colour-forming.

The precursors of these various colour-forming and other impurities are difficultly separable from phenol by ordinary fractional distillation methods; at the temperatures to which the phenol is subjected during fractional distillation operations, the conversion of the

precursors takes place to a certain extent in the still itself whilst an appreciable part of the precursors distill over with the phenol, with the result that the phenol fractions obtained are still contaminated. In the process of the present invention the precursors are converted to benzofurans, and other condensation products, and these are all subsequently separated from the phenol.

The starting material for the process of the present invention may be crude phenol, produced by the decomposition of cumene hydroperoxide, or the phenol which has already been purified to a degree which satisfies the requirements of the British Standard Specification and/or the U.S. Pharmacopeia, but which still contains traces of colour-forming impurities which cannot be removed by conventional methods and which may make the phenol unsuitable for certain applications. It is preferred to use as the starting material phenol which has been treated, for instance by fractional distillation of the washed and/or neutralised decomposition reaction product, for the removal of most of the lower boiling materials, such as acetone, cumene, and α -methylstyrene and/or most of the higher-boiling materials such as acetophenone and phenyl dimethyl carbinol. The phenol may be either in the dry state or it may be diluted with water which enables it to be pumped at ordinary temperatures as a liquid and avoids solidification on cold surfaces.

The treatment of the phenol to convert any α -hydroxy carbonyl compound present to a benzofuran may be carried out by heating the phenol in the liquid or vapour phase to an elevated temperature, for instance at least 40°C ., and preferably between 100° and 400°C . The process may be carried out in the absence of any catalytic agents, or in the presence of a catalytically active material such as activated alumina; aluminium silicates, such as acid- or alkali-treated pumice and porcelain; acidic or basic ion-exchange resins; mineral acids such as sulphuric acid and phosphoric acid especially in the presence of iron; strong organic acids, such as *p*-toluene sulphonic acid; and surface-active earths such as montmorillonites, also known as Fullers' Earth, bentonite, Florida Earth, and attapulgite.

In the case of the vapour phase heat treatment according to the process of the invention, this may be carried out in any suitable manner, for instance by passing the vaporised phenol through an unpacked tube at the desired temperature, but it is preferred to carry out the heat treatment in the presence of a catalytically active material such as those set out above. If desired the heat treatment may be carried out in the presence of catalytically active materials when the lower temperatures in the range set forth are used, and in the absence of such materials at the higher

temperatures. Inert diluents may be used if desired. The heat treatment is preferably carried out in the temperature range 182°C . to 400°C . and at atmospheric pressure. Reduced or increased pressures may be employed if desired, and reduced pressures may be particularly suitable where low temperatures, such as 150° — 182°C . are being used.

In the case of the liquid phase heat treatment according to the process of the invention, it is preferred to use a surface-active earth such as the montmorillonites, also known as Fullers' Earths, bentonites, Florida Earths and attapulgites. They are preferably used in the acid-activated state, although non-acid-activated earths, or earths which have been activated by alkali or heat-treatment may also be used. As examples of such surface-active earths available commercially which are acid-activated may be mentioned the Fullers' Earths 237 SW, Fulmont 500, Fulmont 711 and Fulmont 800 marketed by the Fullers' Earth Union Ltd., Redhill, Surrey. The word "Fulmont" is a Registered Trade Mark. Also marketed by the Fullers' Earth Union is Fulbent 182 an alkali-treated earth or bentonite. Surface-active earths which have been activated by heat-treatment include Florex XXF (a Fullers' Earth) marketed by the Foridin Company, U.S.A., Attapulgis 50—248—52A and 50—248—52C (attapulgites) marketed by the Attapulgis Clay Company, U.S.A. The word "Florex" is a Registered Trade Mark. Other types of surface-active earths which, when acid treated, may be used are kieselguhr, pumice and talc although these are less effective than the montmorillonites. Active charcoal is also an effective catalyst in the liquid phase heat treatment. Other catalysts effective in the liquid phase heat treatment are boron trifluoride, the metal halides of the Friedel-Crafts type and the sulphates of the same metals such as aluminium chloride, ferric chloride, nickel chloride, zinc chloride, aluminium sulphate, ferric sulphate and nickel sulphate. The use of ferric chloride is particularly preferred.

The amount of catalyst used in the liquid phase process may be varied between wide limits, for instance between 0.1 and 10% by weight based on the weight of phenol. The temperatures which may be used in the liquid phase treatment will normally lie in the range 40° to 182°C ., that is between the melting-point and boiling point of pure phenol at atmospheric pressure. Higher temperatures may be used if desired, for instance by operating the system under increased pressures. Reduced pressures may also be used. It is preferred to operate between about 100° and 182°C ., at atmospheric pressure. If desired the treatment may be carried out in the presence of a suitable solvent for phenol for instance aromatic hydrocarbons such as cumene. The length of time over which the

treatment may be applied may vary within wide limits. Periods of about 5 to 30 minutes have been found to be suitable, but longer or shorter periods may be used if desired. In general the longer times are used with the lower temperatures, and *vice-versa*. The liquid phase treatment may be carried out in a batchwise or continuous manner. In the former case the process is preferably carried out in a well agitated vessel to ensure mixing and efficient contacting of the earth with the liquid phenol. The treatment may be repeated if desired using a fresh sample of surface-active earth, in the case of highly contaminated phenols. Alternatively, the phenol may be made to flow over a fixed or moving bed of the surface-active earth.

After the phenol has been subjected to conditions which will cause the condensation of the aliphatic α -hydroxy carbonyl compound with phenol to form benzofurans, the phenol is separated from the benzofurans and from the other impurities which have been formed at the same time. This may be carried out in any suitable manner for example by extractive distillation in the presence of a suitable solvent or by neutralisation of the phenol with alkali, followed by extraction of the benzofurans with a solvent or by steam distillation. It is preferred to subject the phenol to extractive distillation in the presence of water, whereby the benzofurans are removed as an overhead fraction, and the phenol is removed as an intermediate or bottom fraction. The extractive distillation is preferably carried out in a continuous manner, for instance by feeding a solution or mixture of the phenol and water continuously into a column up which a similar mixture is refluxing, removing the benzofurans overhead as an azeotrope with water containing not more than a minor proportion of the phenol, separating the overhead fraction into an aqueous phase and an organic phase, returning part or all of the aqueous phase to the still as reflux, withdrawing part or all of the organic phase, and removing aqueous phenol as an intermediate or bottom fraction. The aqueous phenol may be further treated, if desired, for the recovery of phenol substantially free from higher boiling materials in any suitable manner, preferably by fractional distillation. In one method the wet phenol fraction is first dehydrated, either continuously or in a batchwise manner, by distilling off the water as an azeotrope with some of the phenol, and the rest of the phenol is then taken off as an overhead fraction leaving higher boiling materials as residue. In an alternative method all of the phenol and water are removed together as overhead distillate.

The extractive distillation may also be carried out by feeding the dry phenol continuously into a column up which a mixture of phenol and water is refluxing, removing

the benzofurans overhead as a water azeotrope, returning substantially all of the water as reflux, and withdrawing dry phenol as an intermediate or bottom fraction. The dry phenol may, if desired, be subjected to a further fractional distillation step to separate it from higher boiling materials.

The following examples are given further to illustrate the process of the invention. In the examples the presence of hydroxy acetone was ascertained by the preparation of an osazone with 2,4-dinitrophenylhydrazine, and 2-methylbenzofuran was estimated by gas phase chromatography and/or by spectroscopic methods. In the examples colour measurements were made in a Lovibond Tintometer, using a 1 cm. cell.

EXAMPLE 1.

A crude concentrate of 75% cumene hydroperoxide, obtained by the oxidation of cumene followed by the removal of the unreacted hydrocarbons by flash distillation was decomposed in the presence of 0.4% of concentrated sulphuric acid at 85° C. The final product was neutralised and distilled to give a lower fraction comprising acetone, water and a fraction comprising crude phenol. The phenol fraction was found to contain about 0.35% of hydroxyacetone.

The phenol fraction was first subjected to a process of hydro-extractive distillation to remove all water-strippable material, after which it was dehydrated and distilled, the first fraction of about 10% being discarded. The main phenol fraction passed the B.S.S. specification for pure phenol, but it was found still to contain 0.02% of hydroxyacetone and 70 p.p.m. of 2-methylbenzofuran. On chlorination of a sample of this phenol to the monochlorophenol an objectionable red colour (70 red Lovibond units) was formed.

The phenol was then passed in the vapour phase over alumina at 360° C. at a rate of 1 kg/hr/litre catalyst volume. The resulting product was found to contain 290 p.p.m. of 2-methylbenzofuran, corresponding to a chlorination colour of 290 red Lovibond units, but no hydroxyacetone. This product was treated for the removal of the 2-methylbenzofuran by a straight forward extractive distillation step in the presence of water, by refluxing the phenol through a 40-plate Oldershaw column with 20% by weight of water, followed by dehydration and distillation. The so-treated phenol had a chlorination colour of 0.5 red Lovibond units.

EXAMPLE 2.

A crude concentrate of 75% cumene hydroperoxide, obtained from the oxidation of cumene followed by the removal of the unreacted hydrocarbons by flash distillation, was decomposed as described in Example 1, and the product was distilled to give a crude

phenol fraction, containing about 0.36% hydroxyacetone, but less than 1 p.p.m. of 2-methyl-benzofuran.

5 After standing for several months in metal containers the phenol fraction was found to contain about 300 p.p.m. of 2-methyl-benzofuran, and to have a chlorination colour of 300 red Lovibond units. This phenol was treated by passing over a Fullers' Earth (Grade 10 3H2, marketed by the Fullers' Earth Union Limited) in the vapour phase at 190—194° C. The product contained over 1000 p.p.m. of 2-methyl-benzofuran, which was then removed by extractive distillation in the presence of water as described in Example 1. 15 After dehydration and distillation the final product had a chlorination colour of 0.1 red Lovibond units.

EXAMPLE 3.

20 A sample of phenol obtained by the oxidation of cumene and the decomposition of the resulting hydroperoxide, was extractively distilled in the presence of water, dehydrated and distilled to give a product which had an intense red colour on sulphonation (absorbing at 5040 Å) which was not due to the presence of either hydroxyacetone (5140 Å) or 2-methyl-benzofuran (4860 Å).

25 A sample of this phenol was treated by a process for converting hydroxyacetone into 2-methyl-benzofuran, by vapour phase heat-treatment over a Fullers' Earth catalyst (Grade 249SW, Fullers' Earth Union Limited) at 192—194° and was subsequently subjected to extractive distillation in the presence of water 30 followed by fractionation. On sulphonation of the resulting phenol, the product had a colour which was ten times less intense than the original sulphonation colour, and was no longer objectionable. 40

EXAMPLE 4.

A sample of phenol, produced by the decomposition of cumene hydroperoxide, was found to have a Lovibond colour index, on chlorination under standard conditions to the monochlorophenol stage, of 72 red units. The phenol was vapourised into a glass tube containing a pre-heating section packed with 45 porcelain beads and a reacting section packed with 225 mls. of 8—20 mesh alumina, which had been pre-treated by heating to 900° C. for 7 hours. The phenol was fed in at a rate of 90 to 110 g./hr. and the alumina-packed section of the tube was kept at 360—370° C. 50

55 The heat treated phenol was a dark brown colour and on chlorination to the monochlorophenol stage was found to have a Lovibond colour index of about 140 red units. Thus the heat treatment alone increased the amount of colour by a factor of about 2. 60

The heat treated phenol (2000 g.) was refluxed up a 40-plate Oldershaw column with 500 g. of water to attain equilibrium on the

plates, and then a two-phase fraction amounting to 40 g. was slowly distilled out. The kettle contents were then dehydrated by distillation of the water-phenol azeotrope up a 15-plate Oldershaw column, after which the dried phenol was distilled off overhead leaving higher boiling materials in the kettle. On chlorination this phenol had a Lovibond colour index of 0.4 red units. 65 70

Thus, the combined steps of heat treatment over alumina at 350—370° C., hydro-extractive distillation, and recovery of the phenol from higher boiling materials, lowered the red colour by a factor of 180. 75

EXAMPLE 5.

A further sample of the phenol used in Example 4 which had a Lovibond colour index on chlorination of 72 red units, was diluted with one quarter of its weight of water and heat treated in apparatus similar to that described in Example 4, the alumina packed section of the tube being kept at 360—370° C. and the feed rate being 80 g./hr. The heat-treated aqueous phenol was a dark green fluorescent liquid. This phenol was subjected to a hydro-extractive distillation, dehydration and distillation as described in Example 4. 80 85 90

On chlorination the final product phenol had a Lovibond colour index of less than 0.1 red units. Thus, heat treatment of phenol in the presence of steam over alumina at 360—370° C. followed by hydro-extractive distillation, dehydration and distillation lowered the red colour by a factor of over 700. 95

EXAMPLE 6.

A further sample of the phenol used in Example 4 was passed through the heat treatment apparatus of Example 4 at a rate of 80 to 120 g./hr. and at a temperature of 230° C. This phenol was then refluxed in a 50-plate column with 20% of added water, the aqueous distillate being returned continuously, but the oil phase of the distillate being retained in a trap at the top of the column. Subsequently, the wet phenol was dehydrated in the same column by the removal of both the aqueous and oil distillates. The head of the column was then changed to enable the phenol to be taken off overhead, and the phenol was finally distilled over at a very low reflux ratio. 100 105 110 115

The final pure phenol on chlorination had a Lovibond colour index of less than 0.1 red units.

EXAMPLE 7.

A sample of cumene-process phenol which had a chlorination colour index of 72 red units, was heat treated in apparatus similar to that described in Example 5 packed entirely with plain porcelain beads at a temperature of 260—290° C. The phenol was fed in at a rate of 200 g./hr. The heat treated phenol 120 125

was submitted to hydro-extractive distillation, dehydration and distillation as described in Example 4, and on chlorination this phenol had a Lovibond colour index of 2.5 red units.

- 5 By way of comparison with this example, when a sample of the same phenol was submitted to the same treatment but omitting the heat treatment step, the product had a colour index of 16 red units.

10 **EXAMPLE 8.**

A further sample of the phenol used in Example 7 was passed through 1.8 litres of Grade 3H₂, 8—20 mesh, acid activated Fullers' Earth at a rate of approximately 600

- 15 g./hr. and an average temperature of 195° C. After working up by hydro-extractive distillation, dehydration and distillation as described in Example 4, this phenol had a chlorination colour index of less than 0.5 red units.

20 **EXAMPLE 9.**

A sample of phenol, produced by the decomposition of cumene hydroperoxide, was found to have a colour index on chlorination under standard conditions to the monochlorophenol stage, of 72 red units, and a colour index on sulphonation under standard conditions of 80 red units. The phenol was shaken at the boiling point (182° C.) with 5% by weight of an acid Fullers' Earth (Grade SW 237) for ten minutes. The Fullers' Earth was filtered off and the filtered phenol was refluxed through a 40-plate Oldershaw column with 20% by weight of water after which a small quantity of distillate was taken off at a high reflux ratio. The aqueous phenol obtained from the base of this column was dehydrated by distillation of the water/phenol azeotrope through a 20-plate Oldershaw column, after which the dried phenol was distilled off overhead leaving the higher boiling materials in the kettle. On chlorination under the standard conditions to the monochlorophenol stage, this phenol had a colour index of 0.5 red units, and on sulphonation under the standard conditions a colour index of 2.8 red units.

45 **EXAMPLE 10.**

- 50 The process described in Example 9 was repeated using an alkaline Fullers' Earth (Fulbent 182). The product phenol had a chlorination colour index of 1 red unit, and a sulphonation colour index of 4.3 red units.

55 **EXAMPLE 11.**

- The process described in Example 9 was repeated on a different sample of phenol produced by the decomposition of cumene hydroperoxide. The untreated phenol had a chlorination colour index of 16 red units. After treatment according to the process of the present invention the chlorination colour index of the phenol was 0.2 red units.

EXAMPLE 12.

The process described in Example 9 was repeated on the same sample of phenol, except that the phenol was contacted with the Fullers' Earth at a temperature of 45—50° C., and for a period of 30 minutes. After this treatment the phenol was subjected to hydro-extractive distillation, dehydration and distillation as described in Example 9. The chlorination colour index of the final product was 6.4 red units.

EXAMPLE 13.

A crude phenol produced by the decomposition of cumene hydroperoxide, and containing about 3.4% of hydrocarbons, mainly cumene and α -methylstyrene, when purified by extractive distillation followed by dehydration and distillation only, had a chlorination colour index of 15 red units. A sample of this crude phenol was refluxed at 155° C. for ten minutes with 5% by weight of an acid Fullers' Earth (Grade SW 237). The phenol was then subjected to hydro-extractive distillation, dehydration and distillation as described in Example 9. The final product phenol had a chlorination colour index of about one red unit.

EXAMPLE 14.

A phenol prepared by the cleavage of cumene hydroperoxide in methyl ethyl ketone as solvent was found to contain 6130 p.p.m. of acetyl methyl carbinol (acetoin), and on chlorination to the monochlorophenol stage had a Lovibond colour index of 230 red units.

After refluxing this phenol with 5% by weight of Fullers' Earth for 30 minutes, the treated phenol was found to contain 2600 p.p.m. of 2,3-dimethyl benzofuran, identified by its peak on a gas phase chromatogram, its mass spectrum and its spectral characteristics in the U.V. and I.R. On chlorination to the mono-chlorophenol stage the treated phenol had a Lovibond colour index of 1550 red units. After being submitted to an extractive distillation in the presence of water the phenol was found to contain substantially no benzofuran, and after a further distillation step the distillate gave substantially no red colour on chlorination.

EXAMPLE 15.

A sample of phenol produced by the decomposition of cumene hydroperoxide, when chlorinated to the monochloro stage, had a red colour of about 92 red Lovibond units. The phenol was refluxed for 30 minutes at atmospheric pressure with 5% by weight of an acid Fullers' Earth (Grade 237 SW). The earth was then filtered off from the phenol. A sample of the treated phenol was chlorinated to the monochloro stage, when a red colour developed having a Lovibond colour index of 1140 red units. 18% by weight of water and 1% by weight of cumene were added to the

treated phenol, and the mixture was subjected to a continuous extractive distillation in a 45 tray glass Oldershaw column, the head temperature being maintained at 98–99° C. and the kettle temperature at 105–106° C., the feed tray being 30 trays above the kettle. The head product was condensed, when it separated into two layers. The upper (hydrocarbon) layer was removed as product and the lower (aqueous) layer was returned as reflux to the column. A sample of the kettle product was collected and dehydrated and distilled by batch distillation in a 15 tray glass Oldershaw column. The main dry phenol fraction had a red colour after chlorination to the monochlorophenol stage having a Lovibond colour index of less than 1 red unit.

EXAMPLE 16.

A sample of crude phenol, as used in Example 13, was passed in the vapour phase at a rate of 200 millilitres (liquid)/hour over 425 millilitres of granular alumina in a glass tube heated to 205–210° C. The condensed product was diluted with 18% by weight of water and given a continuous hydroextractive distillation followed by a batch dehydration and distillation as in Example 15. The main dry phenol fraction had a red colour after chlorination to the monochloro stage of approximately 2 red Lovibond units.

EXAMPLE 17.

A sample of crude phenol, as used in Example 13, was pumped at a rate of 200 millilitres per hour in the liquid phase through a steel tower containing 250 millilitres of silica/alumina cracking catalyst maintained at 190° C., a relief valve on the exit being set at 80 p.s.i.g. to maintain the phenol in the liquid phase. The heat treated product was diluted with 18% of water and given a continuous extractive distillation, followed by a batch dehydration and distillation as in Example 15. The main dry phenol fraction had only a weak red colour when chlorinated under standard conditions to the monochloro stage, equivalent to about 0.6 red Lovibond units.

By way of comparison with the above examples the following experiments are given to illustrate the effect of heat treatment and hydro-extractive distillation carried out separately.

EXPERIMENT A.

A further sample of the phenol used in Example 4 was diluted with 20% of its weight of water. This enabled it to be handled as a liquid at ordinary temperatures, and it was heat treated in the apparatus described in Example 4, the feed rate being 80 g./hr. and the alumina packed section of the tube being kept at 360–270° C. The heat treated phenol was a dark green fluorescent liquid, and after dehydration and distillation (i.e. with no

hydro-extractive distillation) the distilled phenol was colourless, but had a chlorination colour of 52 red Lovibond units.

Thus, heat treatment followed by distillation reduced the red colour by a factor of 1.4 only.

EXPERIMENT B.

A further sample of the phenol used in Example 4 (2000 g.) was refluxed up a 40-plate Oldershaw column with 500 g. of water for 20 hours to attain equilibrium on the plates, and then a two-phase fraction amount to 40 g. was slowly distilled out. The kettle contents were then dehydrated by distillation of the water/phenol azeotrope up a 15-plate Oldershaw column, followed by a distillation of the dried phenol overhead.

On chlorination this phenol had a Lovibond colour index of 16 red units. Thus the step of hydroextractive distillation not preceded by heat treatment lowered the red colour by a factor of only 4.5.

EXPERIMENT C.

A sample of the phenol used in Example 9 was refluxed at 182° C. with 5% by weight of Fullers' Earth (Grade SW 237) for ten minutes. The Fullers' Earth was filtered off, and the phenol was then fractionated at atmospheric pressure in a 40-plate Oldershaw column. After 40% of the phenol had been distilled off overhead, the chlorination colour index of the distillate then distilling was 64 red units.

EXPERIMENT D.

A sample of phenol derived from the oxidation of cumene and the decomposition of the resulting hydroperoxide, was subjected to extractive distillation in the presence of water followed by fractionation, and was found to contain 0.02% of hydroxyacetone and 70 p.p.m. of 2-methyl-benzofuran. This sample was subjected to a further purification by extractive distillation in the presence of water followed by fractional distillation. The distilled phenol still contained 10 p.p.m. of 2-methyl-benzofuran. After storing at 60° C. in a mild steel vessel in the presence of 0.01% of phosphoric acid for 1 month, the amount of 2-methyl-benzofuran had increased to 90 p.p.m.

EXAMPLE 18.

Cumene was oxidised to the hydroperoxide and the hydroperoxide was subjected to acid cleavage. The acid catalyst in the cleavage mixture was neutralised and the mixture was separated from the products of the neutralisation reaction. The neutralised cleavage mixture was subjected to fractional distillation in a series of columns. In the first column acetone was taken off overhead, leaving as bottoms product a mixture of phenol, some cumene and α -methyl styrene, and high boiling material composed primarily of acetophenone, dimethyl-phenyl carbinol and cumyl

phenol. This bottoms product was separated in the next column into an overhead crude phenol fraction and a high boiling residue. The crude phenol fraction was then subjected to steam distillation in a third column to remove overhead azeotropes of water with α -methyl styrene and cumene, and leave a crude phenol bottoms product. This product was then stored in a steel container.

The stored phenol contained 41 parts per million of 2-methylbenzofuran, as determined by ultra violet analysis, and to it was added 0.5% by weight of ferric chloride. The resulting mixture had a pH of 2.8 and was maintained at 120° C. for 70 hours, after which the content of 2-methylbenzofuran was 268 p.p.m.

A sample of the treated phenol was separated into two portions, one of which was subjected to ordinary batch distillation, with the charge being added to the steel pot. The other portion was fractionally steam distilled using a modified inverted batch still technique, in which distilled water was charged to the still pot and brought to reflux, and then the treated phenol was pumped continuously into the top of the still while maintaining water reflux. Thus, all of the phenol was contacted with steam as it flowed down and across all of the trays of the column. After all the charge had been added, distillation was carried out in the normal manner.

A phenol obtained from each distillation was chlorinated to the mono-chlorophenol stage. The phenol from ordinary distillation had a colour of about 120 red Lovibond units, whereas that from the steam distillation contained 8 p.p.m. of 2-methylbenzofuran and had a colour of about 3 red Lovibond units.

EXAMPLE 19.

A neutralised cumene hydroperoxide cleavage mixture was distilled as in Example 18 to obtain an acetone fraction and an overhead crude phenol fraction. The crude phenol fraction was contacted with 1.5% of aluminium chloride for 0.5 hours at 150° C. After steam distilling as shown in Example 18, the distilled phenol on chlorination exhibited satisfactory colour.

EXAMPLE 20.

To a sample of a stored phenol such as that used in Example 1 were added 0.5% of nickel chloride and sufficient hydrochloric acid to bring the pH of the mixture to 2.0. The mixture was heated at 120° C. for 91 hours, at which time the 2-methyl benzofuran content was 178 p.p.m. After steam distillation as described in Example 18 the distilled product contained 10 p.p.m. of 2-methylbenzofuran and gave a chlorination colour of about 6 red Lovibond units.

Substitution of 0.05% by weight of nickel sulphate for the nickel chloride gave a treated product containing 171 p.p.m. of methyl

benzofuran. After steam distillation the distilled product contained 10 p.p.m. of 2-methylbenzofuran and had a chlorination colour of about 6 red Lovibond units.

WHAT WE CLAIM IS:—

1. The process for the purification of phenol derived from cumene and containing colour forming impurities including aliphatic α -hydroxy carbonyl compounds which comprises subjecting the impure phenol at an elevated temperature to conditions which will cause the substantially complete condensation of the aliphatic α -hydroxy carbonyl compounds with phenol to form benzofurans, and separating the phenol substantially completely from the benzofurans.

2. The process as claimed in Claim 1 wherein the starting material is phenol which has been treated, by fractional distillation of the washed and/or neutralised cumene hydroperoxide decomposition reaction product, for the removal of substantially all of the lower and higher boiling materials.

3. The process as claimed in either of the preceding claims wherein the conditions comprise heating the impure phenol to an elevated temperature in the liquid or vapour phase.

4. The process as claimed in Claim 3 wherein the impure phenol is heated to a temperature between 100° and 400° C.

5. The process as claimed in Claim 3 wherein the impure phenol is heated in the presence of a condensation catalyst.

6. The process as claimed in Claim 5 wherein the catalyst is activated alumina, an aluminium silicate, an acidic or basic ion-exchange resin, a mineral acid, a strong organic acid, or a surface-active earth.

7. The process as claimed in Claim 5 wherein the catalyst is iron and sulphuric acid or phosphoric acid.

8. The process as claimed in Claim 5 wherein the impure phenol is heated in the liquid phase in the presence of a montmorillonite earth.

9. The process as claimed in Claim 8 wherein the impure phenol is heated to a temperature between 100° and 182° C. at atmospheric pressure.

10. The process as claimed in any of the preceding claims wherein the impure phenol is separated from the benzofurans by extractive distillation in the presence of water to remove the benzofurans as an overhead fraction and the purified phenol as an intermediate or bottom fraction.

11. The process as claimed in Claim 10 wherein the extractive distillation is carried out in a continuous manner.

12. The process as claimed in Claim 10 wherein the benzofurans are removed overhead as an azeotrope with water containing not more than a minor proportion of the phenol, the overhead fraction is separated into an

- aqueous phase and an organic phase, part or all of the aqueous phase is returned to the still as reflux, part or all of the organic phase is withdrawn, and aqueous phenol is removed as an intermediate or bottom fraction.
13. The process as claimed in Claim 12 wherein the aqueous phenol is fractionally distilled to recover dry phenol free from higher boiling materials.
14. The process as claimed in Claim 10 wherein the extractive distillation is carried out by feeding the dry phenol continuously into a column up which a mixture of phenol and water is refluxing, removing the benzofurans overhead as a water azeotrope, returning substantially all of the water to the column as reflux, and withdrawing dry phenol as an intermediate or bottom fraction.
15. The process as claimed in Claim 14 wherein the dry phenol is subsequently subjected to a further fractional distillation step to separate it from higher boiling materials.
16. The process for the purification of phenol derived from cumene and containing colour forming impurities which comprises heating the impure phenol to an elevated temperature in the liquid or vapour phase to cause the substantially complete condensation of the colour forming impurities with phenol, and separating the phenol from the condensation products by extractive distillation in the presence of water to remove the condensation products as an overhead fraction and the phenol as a separate fraction.
17. The process as claimed in Claim 16 wherein the impure phenol is heated in the presence of a condensation catalyst.
18. The process for the purification of phenol substantially as described in the examples.
19. Phenol when produced by a process claimed in any of the preceding claims.
20. The process as claimed in Claim 5 wherein the impure phenol is heated in the liquid phase in the presence as catalyst of a metal halide of the Friedel-Crafts type or a sulphate of the same metals.
21. The process as claimed in Claim 20 wherein the catalyst is ferric chloride.
22. The process as claimed in Claims 3 or 4 wherein the impure phenol is heated in the liquid phase under superatmospheric pressure in the absence of a catalyst.
- JOHN HARRY,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

No. 6855, A.D. 1958.

Purification of Phenol

55 We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare this invention to be described in the following statement:—

60 The present invention relates to the purification of phenols and in particular to the purification of phenols derived from cumene.

The production of phenol by the oxidation of cumene and the decomposition of the resulting hydroperoxide is well known. The phenol produced in this process can be purified by conventional methods to a degree which satisfies the exacting requirements of the British Standard Specification and of the U.S. Pharmacopeia. However, some samples of phenol produced in this way, while conforming to these specifications, still contain impurities which render them unsuitable for certain purposes. For instance, it has been found that some samples of highly purified phenol give an undesirable colour when subjected to chlorination; particularly to the mono- and penta-chlorophenols. Another important application of phenol is in the manufacture of synthetic tannins, which involves the sulphonation of the phenol, and it has been found that some samples of highly purified phenol give an undesirable colour when subjected to sulphonation, which makes them unsuitable for such application.

Various methods have been used in attempts to remove from the phenol contaminants such as those which cause colour formation on chlorination and/or sulphonation. Fractional distillation of the phenol usually results in some improvement, but the phenol still gives sufficient colour on chlorination and/or sulphonation to render it unsuitable for these uses. Similarly, hydro-extractive distillation of the phenol followed by fractional distillation does not always remove all of the colour-producing impurities. Other methods which have been tried include heat treatment of the phenol, for instance at 300° to 350° C., but this has been found to result in substantially increased colour formation when the phenol is subsequently chlorinated. If the heat treatment is followed by a fractional distillation step some purification is achieved but the phenol still gives sufficient colour on chlorination and/or sulphonation to render it unsuitable for applications involving such treatments.

According to the present invention the process for the purification of phenol produced by the decomposition of cumene hydroperoxide comprises subjecting the phenol to heat treatment in the vapour phase at temperatures in the range 150°—400° C.; separating, by distilling the heat-treated phenol in the presence of water, an overhead frac-

tion containing materials boiling below the boiling point of the phenol/water azeotrope, and an aqueous phenol fraction; and recovering from the aqueous phenol fraction phenol substantially free from materials boiling higher than the phenol/water azeotrope.

The starting material for the process of the present invention may be crude phenol, produced by the decomposition of cumene hydroperoxide, or the phenol which has already been purified to a degree which satisfies the requirements of the British Standard Specification and/or the U.S. Pharmacopeia, but which still contains trace impurities which cannot be removed by prior art methods. It is preferred to use as the starting material phenol which has been treated, for instance by fractional distillation of the washed and neutralised decomposition reaction product, for the removal of most of the lower boiling materials, such as acetone, cumene, and α -methylstyrene, and/or most of the higher-boiling materials such as acetophenone and phenyl-dimethyl carbinol. The phenol submitted to the heat treatment may be either in the dry state or it may be diluted with water, which enables it to be pumped at ordinary temperatures as a liquid and avoids solidification on cold surfaces.

The vapour phase heat treatment according to the process of the invention may be carried out in any suitable manner, for instance by passing the vaporised phenol through an unpacked tube at the desired temperature. In a preferred embodiment, however, the heat treatment is carried out in the presence of a catalytically active material such as activated alumina, acid-treated pumice, acidic surface active clays, for instance Fullers' Earth, acidic ion-exchange resins, and the like. If desired the heat treatment may be carried out in the presence of catalytically active materials when the lower temperatures in the range set forth are used, and in the absence of such materials at the higher temperatures. The heat treatment is preferably carried out in the temperature range 180° to 400° C. and at atmospheric pressure. Reduced or increased pressures may be employed if desired, and reduced pressures may be particularly suitable where low temperatures, such as 150°—180° C., are being used.

The separation, by distillation of the heat-treated phenol in the presence of water, of an overhead fraction may be carried out in any suitable manner, for instance by mixing with the phenol sufficient water to enable the mixture or solution to be refluxed in a kettle under an efficient distillation column with the kettle temperature below that at which phenol boils at the prevailing pressure, i.e. within the range 100°—180° at 760 mm., taking off an overhead fraction containing materials boiling below the boiling point of the phenol/water azeotrope and withdrawing aqueous phenol

from the kettle. Alternatively, a solution or mixture of water and phenol may be fed continuously into a column up which a similar mixture or solution is refluxing, and portions withdrawn from the reflux and from the lower part of the column in such a manner as to keep the overall volume of liquid in the column constant and to remove at the head any steam-volatile impurities.

The aqueous phenol remaining after separation of the overhead fraction may be treated for the recovery of phenol substantially free from higher boiling materials in any suitable manner, for instance by distillation, fractional crystallisation or adsorption methods. However it is preferred to recover the phenol by fractional distillation. Preferably the wet phenol fraction is first dehydrated either continuously or in a batchwise manner, by distilling off the water as an azeotrope with some of the phenol, and the rest of the phenol is then taken off as an overhead fraction leaving higher boiling materials as residue. In an alternative method all of the phenol and water are removed together as overhead distillate.

The following examples are given further to illustrate the process of the present invention.

EXAMPLE 1.

A sample of phenol, produced by the decomposition of cumene hydroperoxide, was found to have a Lovibond colour index, on chlorination under standard conditions to the monochlorophenol stage, of 72 red units. The phenol was vapourised into a glass tube containing a pre-heating section packed with porcelain beads and a reacting section packed with 225 mls. of 8—20 mesh alumina, pre-treated by heating to 900° C. for 7 hours. The phenol was fed in at a rate of 90 to 110 g./hr. and the alumina-packed section of the tube was kept at 360—370° C.

The heat treated phenol was a dark brown colour and on chlorination to the monochlorophenol stage was found to have a Lovibond colour index of about 140 red units. Thus the heat treatment alone increased the amount of colour by a factor of about 2.

The heat treated phenol (2000 g.) was refluxed up a 40-plate Oldershaw column with 500 g. of water for 20 hours to attain equilibrium on the plates, and then a two-phase fraction amounting to 40 g. was slowly distilled out. The kettle contents were then dehydrated by distillation of the water-phenol azeotrope up a 15-plate Oldershaw column, after which the dried phenol was distilled off overhead leaving higher boiling materials in the kettle. On chlorination this phenol had a Lovibond colour index of 0.4 red and 0.04 yellow units.

Thus, the combined steps of heat treatment over alumina at 360—370° C., hydro-extrac-

tive distillation, and recovery of the phenol from higher boiling materials, lowered the red colour by a factor of 180.

EXAMPLE 2.

5 The process of Example 1 was repeated on a sample of another batch of phenol produced in the same way, which had an initial chlorination colour index of 72 red, and 4.0 yellow Lovibond units. The phenol was heat treated in the same apparatus as described in Example 1, the feed rate being 30 g./hr. and the alumina-packed section of the tube being kept at 350° C. After heat treatment the phenol had a chlorination colour of 215 red and 0.0 yellow units. The heat treated phenol was submitted to a hydro-extractive distillation, dehydration and distillation as described in Example 1. On chlorination this phenol had a Lovibond colour index of 0.5 red and 20 0.1 yellow units.

EXAMPLE 3.

A further sample of the phenol used in Example 2 was submitted to the process described in Example 2, the heat treatment being carried out at 320° C. and at a feed rate of 190 g./hr. After the heat treatment the phenol had a chlorination colour index of 280 red and 0.0 yellow units. After hydro-extractive distillation, dehydration and distillation as described in Example 1, the phenol had a chlorination colour index of 1.3 red and 0.4 yellow units.

EXAMPLE 4.

A further sample of the phenol used in Example 1, which had a Lovibond colour index on chlorination of 72 red units, was diluted with one quarter of its weight of water and heat treated in apparatus similar to that described in Example 1, the alumina packed section of the tube being kept at 360—370° C. and the feed rate being 80 g./hr. The heat-treated aqueous phenol was a dark green fluorescent liquid. This phenol was subjected to a hydro-extractive distillation, dehydration and distillation as described in Example 1.

On chlorination the final product phenol had a Lovibond colour index of less than 0.1 red units.

Thus, heat treatment of phenol in the presence of steam over alumina at 360—370° C. followed by hydro-extractive distillation, dehydration and distillation lowered the red colour by a factor of over 700.

EXAMPLE 5.

55 A further sample of the phenol used in Example 1 was passed through the heat treatment apparatus of Example 1 at a rate of 80 to 120 g./hr. and at a temperature of 230° C. This phenol was then refluxed for 60 17 hours in a 50-plate column with 20% of added water, the aqueous distillate being re-

turned continuously, but the oil phase of the distillate being retained in a trap at the top of the column. Subsequently, the wet phenol was dehydrated in the same column by the removal of both the aqueous and oil distillates. The head of the column was then changed to enable the phenol to be taken off overhead, and the phenol was finally distilled over at a very low reflux ratio.

The final pure phenol on chlorination had a Lovibond colour index of less than 0.1 red units.

EXAMPLE 6.

A further sample of the phenol used in Example 2, which had a chlorination colour index of 72 red and 4.0 yellow units, was heat treated in apparatus similar to that described in Example 1, packed entirely with plain porcelain beads at a temperature of 260—290° C. The phenol was fed in at a rate of 200 g./hr. The heat treated phenol was submitted to hydro-extractive distillation, dehydration and distillation as described in Example 1, and on chlorination this phenol had a Lovibond colour index of 2.5 red and 0.1 yellow units.

By way of comparison with this example, when a sample of the same phenol was submitted to the same treatment but omitting the heat treatment step, the product had a colour index of 16 red units.

EXAMPLE 7.

A further sample of the phenol used in Example 2 was passed through 1.8 litres of Grade 3H₂, 8—20 mesh, acid activated Fullers' Earth at a rate of approximately 600 g./hr. and an average temperature of 195° C.

After working up by hydro-extractive distillation, dehydration and distillation as described in Example 1, this phenol had a chlorination colour index of less than 0.5 red and 0.1 yellow units.

By way of comparison with the above examples the following experiments are given to illustrate the effect of heat treatment and hydro-extractive distillation carried out separately.

EXPERIMENT A.

A further sample of the phenol used in Example 1 was diluted with 20% of its weight of water. This enabled it to be handled as a liquid at ordinary temperatures, and it was heat treated in the apparatus described in Example 1, the feed rate being 80 g./hr. and the alumina packed section of the tube being kept at 360—370° C. The heat-treated phenol was a dark green fluorescent liquid, and after dehydration and distillation (i.e. with no hydro-extractive distillation) the distilled phenol was colorless, but had a chlorination colour of 52 red Lovibond units.

Thus, heat treatment followed by distillation reduced the red colour by a factor of 1.4 only.

EXPERIMENT B.

A further sample of the phenol used in Example 1 (2000 g.) was refluxed up a 40-plate Oldershaw column with 500 g. of water for 20 hours to attain equilibrium on the plates, and then a two-phase fraction amounting to 40 g. was slowly distilled out. The kettle contents were then dehydrated by distillation of the water/phenol azeotrope up a 15-plate Oldershaw column, followed by a distillation of the dried phenol overhead.

On chlorination this phenol had a Lovibond colour index of 16 red and 1.5 yellow units.

Thus the step of hydro-extractive distillation not preceded by heat treatment lowered the red colour by a factor of only 4.5.

When the process of Experiment B was repeated on the phenol used in Example 2 the chlorination colour of the dehydrated phenol was 32 red and 2.0 yellow units. After the dehydrated phenol had been distilled to remove an overhead phenol fraction, the latter had a chlorination colour of 8 red and 0.8 yellow units.

JOHN HARRY,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

No. 7521, A.D. 1958.

Purification of Phenol

25 We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare this invention to be described in the following statement:—

30 The present invention relates to the purification of phenols and in particular to the purification of phenol derived from cumene.

The production of phenol by the oxidation of cumene and the decomposition of the resulting hydroperoxide is well known. The phenol produced in this process can be purified by conventional methods to a degree which satisfies the exacting requirements of the British Standard Specification and of the U.S. Pharmacopeia. However, some samples of phenol produced in this way, while conforming to these specifications, still contain impurities which render them unsuitable for certain purposes. For instance, it has been found that some samples of highly purified phenol give an undesirable colour when subjected to chlorination; particularly to the mono- and penta-chlorophenols. Another important application of phenol is in the manufacture of synthetic tannins, which involves the sulphonation of the phenol, and it has been found that some samples of highly purified phenol give an undesirable colour when subjected to sulphonation, which makes them unsuitable for such application.

Various methods have been used in attempts to remove from the phenol contaminants such as those which cause colour formation on chlorination and/or sulphonation. Fractional distillation of the phenol usually results in some improvement, but the phenol still gives sufficient colour on chlorination and/or sulphonation to render it unsuitable for these uses. Similarly, hydroextractive distillation of the phenol followed by fractional distillation does not always remove all of the colour-producing impurities. Other methods which have been tried include heat treatment of the phenol, for instance at 300° to 350° C., but this has been found to result in substantially increased colour formation when the

phenol is subsequently chlorinated. If the heat-treatment is followed by a fractional distillation step some purification is achieved but the phenol still gives sufficient colour on chlorination and/or sulphonation to render it unsuitable for applications involving such treatments.

According to the present invention the process for the purification of phenol produced by the decomposition of cumene hydroperoxide comprises contacting the phenol in the liquid phase with a surface-active earth at an elevated temperature; separating, by distilling the phenol in the presence of water, an overhead fraction containing materials boiling below the boiling point of the phenol/water azeotrope, and an aqueous phenol fraction; and recovering from the aqueous phenol fraction, phenol substantially free from materials boiling higher than the phenol/water azeotrope.

The starting material for the process of the present invention may be crude phenol, produced by the decomposition of cumene hydroperoxide, or phenol which has already been purified to a degree which satisfies the requirements of the British Standard Specification and/or the U.S. Pharmacopeia, but still contains trace impurities which cannot be removed by prior art methods. It is preferred to use as the starting material phenol from which most of the lower boiling materials, such as acetone, cumene, and α -methylstyrene, and/or most of the higher boiling materials such as acetophenone and phenyl and dimethyl carbinol have been removed, for instance by fractional distillation of the washed and neutralised decomposition reaction product. The starting material may be either in the dry state or it may be diluted with water, which enables it to be pumped at ordinary temperatures as a liquid and avoids solidification on cold surfaces.

The surface-active earths which it is preferred to use in the liquid phase treatment according to the present invention are the montmorillonites, also known as Fullers'

Earth, bentonites, Florida Earths and attapulgites. They are preferably used in the acid-activated state, although non-acid-activated earths, or earths which have been activated by alkali or heat-treatment may also be used. As examples of such surface-active earths available commercially which are acid-activated may be mentioned FE 237 and SW 237, Fulmont 500, Fulmont 711 and Fulmont 800 (Fullers' Earths) marketed by the Fullers' Earth Union Ltd. Redhill, Surrey. Also marketed by the Fullers' Earth Union is Fulbent 182, an alkali-treated earth or bentonite. Surface-active earths which have been activated by heat-treatment include Florex XXF (A Fullers' Earth) marketed by the Floridin Company, U.S.A. Attapulgis 50—248—52A and 50—248—52C (attapulgis) marketed by the Attapulgis Clay Company, U.S.A. Other types of surface-active earths which, when acid treated, may be used are kieselguhr and talc although these are less effective than the montmorillonites.

The amount of surface-active earth used in the process may be varied between wide limits, for instance between about 0.1 and 10% by weight based on the weight of phenol.

The temperatures which may be used in the liquid phase treatment will normally lie in the range 40° to 182° C., that is between the melting-point and boiling point of pure phenol at atmospheric pressure. Higher or lower temperatures may be used if desired, for instance by operating the system under increased or reduced pressures, or by the addition of a suitable solvent for phenol for instance aromatic hydrocarbons such as cumene. It is preferred to operate between about 98° C. and 182° C. at atmospheric pressure. The length of time over which the treatment may be applied may vary within wide limits. Periods of about 5 to 30 minutes have been found to be suitable, but longer or shorter periods may be used if desired. In general the longer times are used with the lower temperatures, and *vice versa*.

The liquid phase treatment according to the present invention may be carried out in a batchwise or continuous manner. In the former case the process is preferably carried out in a well-agitated vessel to ensure mixing and efficient contacting of the earth with the liquid phenol. The treatment may be repeated if desired using a fresh sample of surface-active earth, in the case of highly contaminated phenols. Alternatively, the phenol may be made to flow over a fixed or moving bed of the surface-active earth.

The separation, by distillation of the surface-active earth-treated phenol in the presence of water, of an overhead fraction may be carried out in any suitable manner, for instance by mixing with the phenol sufficient water to enable the mixture or solution to be refluxed in a kettle under an efficient distil-

lation column with the kettle temperature below that at which phenol boils at the prevailing pressure, i.e. within the range 100°—180° at 760 mm., taking off an overhead fraction containing materials boiling below the boiling point of the phenol/water azeotrope and withdrawing aqueous phenol from the kettle. Alternatively, a solution of mixture of water and phenol may be fed continuously into a column up which a similar mixture or solution is refluxing, and portions withdrawn from the reflux and from the lower part of the column in such a manner as to keep the overall volume of liquid in the column constant and to remove at the head any steam-volatile impurities.

The aqueous phenol remaining after separation of the overhead fraction may be treated for the recovery of phenol substantially free from higher boiling materials in any suitable manner, for instance by distillation, fractional crystallisation or adsorption methods. However, it is preferred to recover the phenol by fractional distillation. Preferably the wet phenol fraction is first dehydrated, either continuously or in a batchwise manner, by distilling off the water as an azeotrope with some of the phenol, and the rest of the phenol is then taken off as an overhead fraction leaving higher boiling materials as residue. In an alternative method all of the phenol and water are removed together as overhead distillate.

The following examples are given further to illustrate the process of the present invention. In the examples the colour of the samples of chlorinated and sulphonated phenol was measured on a Lovibond Tintometer using a 1 cm. cell.

EXAMPLE 1.

A sample of phenol, produced by the decomposition of cumene hydroperoxide, was found to have a colour index on chlorination under standard conditions to the monochlorophenol stage, of 72 red units, and a colour index on sulphonation under standard conditions of 80 red units. The phenol was shaken at the boiling point (182° C.) with 5% by weight of an acid Fullers' Earth (Grade SW 237) for ten minutes. The Fullers' Earth was filtered off and the filtered phenol was refluxed through a 40-plate Oldershaw column with 20% by weight of water for 19 hours, after which a small quantity of distillate was taken off at a high reflux ratio. The aqueous phenol obtained from the base of this column was dehydrated by distillation of the water/phenol azeotrope through a 20-plate Oldershaw column, after which the dried phenol was distilled off overhead leaving the higher boiling materials in the kettle. On chlorination under the standard conditions to the monochlorophenol stage, this phenol had a colour index of 0.5 red units, and on sul-

phonation under the standard conditions a colour index of 2.8 red units.

EXAMPLE 2.

The process described in Example 1 was repeated using an alkaline Fullers' Earth (Fulbent 182). The product phenol had a chlorination colour index of 1 red unit, and a sulphonation colour index of 4.3 red units.

EXAMPLE 3.

The process described in Example 1 was repeated on a different sample of phenol produced by the decomposition of cumene hydroperoxide. The untreated phenol had a chlorination colour index of 16 red units. After treatment according to the process of the present invention the chlorination colour index of the phenol was 0.2 red units.

EXAMPLE 4.

The process described in Example 1 was repeated on the same sample of phenol, except that the phenol was contacted with the Fullers' Earth at a temperature of 45—50° C., and for a period of 30 minutes. After this treatment the phenol was subjected to hydro-extractive distillation, dehydration and distillation as described in Example 1. The chlorination colour index of the final product was 6.4 red units.

EXAMPLE 5.

A crude phenol produced by the decomposition of cumene hydroperoxide, and containing about 3.4% of hydrocarbons, mainly cumene and α -methylstyrene, when purified by extractive distillation followed by dehydration and distillation only, had a chlorination colour index of 15 red units. A sample of this crude phenol was refluxed at 155° C. for ten minutes with 5% by weight of an acid Fullers' Earth (Grade SW 237). The phenol was then subjected to hydro-extractive distillation, dehydration and distillation as described in Example 1. The final product phenol had a chlorination colour index of about one red unit.

By way of comparison with the above examples, a further sample of the phenol used in Example 1 was refluxed at 182° C. with 5% by weight of Fullers' Earth (Grade SW 237) for ten minutes. The Fullers' Earth was filtered off, and the phenol was then fractionated at atmospheric pressure in a 40-plate Oldershaw column. After 40% of the phenol had been distilled off overhead, the chlorination colour index of the distillate then distilling was 64 red units.

JOHN HARRY,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

No. 37324, A.D. 1958.

Purification of Phenol

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare this invention to be described in the following statement:—

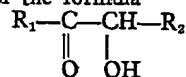
The present invention relates to the purification of phenols and in particular to the purification of phenol derived from cumene.

The production of phenol by the oxidation of cumene and the decomposition of the resulting hydroperoxide is well known. The phenol produced in this process can be purified by conventional methods to a degree which satisfies the exacting requirements of the British Standard Specification and of the U.S. Pharmacopeia. However, some samples of highly purified phenol produced in this way, while conforming to these specifications, still contain impurities which cause the development of an undesired colour when the phenol is subjected to chlorination, particularly to the mono- and penta-chlorophenols, or on sulphonation with concentrated sulphuric acid. These impurities are referred to in this specification as "colour forming impurities".

According to the present invention the process for the purification of phenol derived from cumene and containing colour forming impurities comprises subjecting the phenol

to conditions which will cause the condensation of aliphatic α -hydroxy carbonyl compounds with phenol to form substituted benzofurans, and separating the phenol from the benzofurans.

The invention is based on the discovery that the undesired colour which develops when the phenol is subjected to chlorination and/or sulphonation is at least partially due to the presence of very small quantities of one or more substituted benzofurans in the phenol. It has further been discovered that these substituted benzofurans are formed by the condensation of phenol with various precursors of which the most important appear to be aliphatic α -hydroxy carbonyl compounds, i.e. compounds of the formula



R_1 and R_2 being hydrogen atoms or alkyl groups. Such compounds include hydroxyacetone and acetyl methyl carbinol (acetoin). Thus it is believed that hydroxyacetone condenses with phenol to form 2-methyl-benzofuran, while acetoin condenses with phenol to form 2,3-dimethylbenzofuran. Chlorination and/or sulphonation colour can also be caused by the presence in the phenol of other con-

densation products, which are not substituted benzofurans, also derived from various precursors including aliphatic α -hydroxy carbonyl compounds, such as hydroxyacetone and acetoin, as well as compounds such as diacetyl and mesityl oxide. It has been found that the conditions which will cause the conversion of aliphatic α -hydroxy carbonyl compounds to substituted benzofurans also result in the formation of these other colour-forming condensation products, and in the conversion of the aliphatic α -hydroxy carbonyl compounds in part to impurities which are not colour-forming.

The precursors of these various colour-forming and other impurities are difficultly separable from phenol by ordinary fractional distillation methods; at the temperatures to which the phenol is subjected during fractional distillation operations, the conversion of the precursors takes place to a certain extent in the still itself whilst an appreciable part of the precursors distil over with the phenol, with the result that the phenol fractions obtained are still contaminated. In the process of the present invention the precursors are converted to substituted benzofurans, and other condensation products, and these are all subsequently separated from the phenol.

The starting material for the process of the present invention may be crude phenol, produced by the decomposition of cumene hydroperoxide, or the phenol which has already been purified to a degree which satisfies the requirements of the British Standard Specification and/or the U.S. Pharmacopeia, but which still contains traces of colour-forming impurities which cannot be removed by conventional methods and which may make the phenol unsuitable for certain applications. It is preferred to use as the starting material phenol which has been treated, for instance by fractional distillation of the washed and neutralised decomposition reaction product, for the removal of most of the lower boiling materials, such as acetone, cumene, and α -methylstyrene and/or most of the higher-boiling materials such as acetophenone and phenyl-dimethyl carbinol. The phenol may be either in the dry state or it may be diluted with water which enables it to be pumped at ordinary temperatures as a liquid and avoids solidification on cold surfaces.

The treatment of the phenol to convert any α -hydroxy carbinol compound present to a substituted benzofuran may be carried out by heating the phenol in the liquid or vapour phase to an elevated temperature, for instance at least 40° C., and preferably between 100° and 400° C. The process may be carried out in the absence of any catalytic agents, or in the presence of a catalytically active material such as activated alumina; acid; or alkali-treated pumice; acidic or basic ion-exchange resins; mineral acids such as sulphuric acid

and phosphoric acid especially in the presence of iron; and montmorillonite, also known as Fullers' Earth, bentonite, Florida Earth, and attapulgite.

In the case of the vapour phase heat treatment according to the process of the invention, this may be carried out in any suitable manner, for instance by passing the vaporised phenol through an unpacked tube at the desired temperature, but it is preferred to carry out the heat treatment in the presence of a catalytically active material such as those set out above. If desired the heat treatment may be carried out in the presence of catalytically active materials when the lower temperatures in the range set forth are used, and in the absence of such materials at the higher temperatures. Inert diluents may be used if desired. The heat treatment is preferably carried out in the temperature range 182° to 400° C. and at atmospheric pressure. Reduced or increased pressures may be employed if desired, and reduced pressure may be particularly suitable where low temperatures, such as 150°—182° C., are being used.

In the case of the liquid phase heat treatment according to the process of the invention, it is preferred to use a surface-active earth such as the montmorillonites, also known as Fullers' Earths, bentonites, Florida Earths and attapulgites. They are preferably used in the acid-activated state, although non-acid-activated earths, or earths which have been activated by alkali or heat-treatment may also be used. As examples of such surface-active earths available commercially which are acid-activated may be mentioned FE 237 and SW 237, Fulmont 500, Fulmont 711 and Fulmont 800 (Fullers' Earths) marketed by the Fullers' Earth Union Ltd., Redhill, Surrey. Also marketed by the Fullers' Earth Union is Fulbent 182, an alkali-treated earth or bentonite. Surface-active earths which have been activated by heat-treatment include Florex XXF (a Fullers' Earth) marketed by the Floridin Company, U.S.A., Attapulgis 50—248—52A and 50—248—52C (attapulgitites) marketed by the Attapulgis Clay Company, U.S.A. Other types of surface-active earths which, when acid treated, may be used are kieselguhr and talc although these are less effective than the montmorillonites. Active charcoal is also an effective catalyst in the liquid phase heat treatment. The amount of catalyst used in the liquid phase process may be varied between wide limits, for instance between 0.1 and 10% by weight based on the weight of phenol. The temperatures which may be used in the liquid phase treatment will normally lie in the range 40° to 182° C., that is between the melting-point and boiling point of pure phenol at atmospheric pressure. Higher temperatures may be used if desired, for instance by operating the system under increased pressures. Reduced pressures may also be used. It is

5 preferred to operate between about 100° and 182° C., at atmospheric pressure. If desired the treatment may be carried out in the presence of a suitable solvent for phenol for instance aromatic hydrocarbons such as cumene. The length of time over which the treatment may be applied may vary within wide limits. Periods of about 5 to 30 minutes have been found to be suitable, but longer or shorter periods may be used if desired. In general the longer times are used with the lower temperatures, and *vice-versa*. The liquid phase treatment may be carried out in a batchwise or continuous manner. In the former case the process is preferably carried out in a well agitated vessel to ensure mixing and efficient contacting of the earth with the liquid phenol. The treatment may be repeated if desired using a fresh sample of surface-active earth, in the case of highly contaminated phenols. Alternatively, the phenol may be made to flow over a fixed or moving bed of the surface-active earth.

25 After the phenol has been subjected to conditions which will cause the condensation of the aliphatic α -hydroxy carbonyl compound with phenol to substituted benzofurans, the phenol is separated from the benzofurans and from the other impurities which have been formed at the same time. This may be carried out in any suitable manner using distillation or extraction techniques, but it is preferred to subject the phenol to extractive distillation in the presence of water, for instance by mixing with the phenol sufficient water to enable the mixture or solution to be refluxed in a kettle under an efficient distillation column with the kettle temperature below that at which phenol boils at the prevailing pressure, i.e. within the range 100–180° at 760 mm., taking off an overhead fraction containing materials entrained by the phenol/water azeotrope and withdrawing aqueous phenol from the kettle. Alternatively, a solution or mixture of water and phenol may be fed continuously into a column up which a similar mixture or solution is refluxing, and portions withdrawn from the reflux and from the lower part of the column in such a manner as to keep the overall volume of liquid in the column constant and to remove at the head the impurities entrained by the aqueous vapours.

55 The aqueous phenol remaining after separation of the overhead fraction may be treated for the recovery of phenol substantially free from higher boiling materials in any suitable manner, for instance by distillation, fractional crystallisation on or adsorption methods. However, it is preferred to recover the phenol by fractional distillation. Preferably the wet phenol fraction is first dehydrated, either continuously or in a batchwise manner, by distilling off the water as an azeotrope with some of the phenol, and the rest of the phenol is

then taken off as an overhead fraction leaving higher boiling materials as residue. In an alternative method all of the phenol and water are removed together as overhead distillate.

The following examples are given further to illustrate the process of the invention. In the examples the presence of hydroxy acetone was ascertained by the preparation of an osazone with 2,4-dinitrophenylhydrazine, and 2-methylbenzofuran was estimated by gas phase chromatography and/or by spectroscopic methods.

EXAMPLE 1.

A crude concentrate of 75% cumene hydroperoxide, obtained by the oxidation of cumene followed by the removal of the unreacted hydrocarbons by flash distillation was decomposed by adding it to the product of its own cleavage containing 0.4% of concentrated sulphuric acid at 85° C. The final product was neutralized with aqueous sodium carbonate and distilled to give a lower fraction comprising acetone, water and a fraction comprising crude phenol. The phenol fraction was found to contain about 0.35% of hydroxyacetone.

The phenol fraction was first subjected to a process of hydro-extractive distillation to remove all water-strippable material, after which it was dehydrated and distilled, the first fraction of about 10% being discharged. The main phenol fraction passed the B.S.S. specification for pure phenol, but it was found still to contain 0.02% of hydroxyacetone and 70 p.p.m. of 2-methylbenzofuran. On chlorination of this phenol to the monochlorophenol an objectionable red colour was formed.

The phenol was then passed over alumina at 260° C. at a rate of 1 kg/hr/litre catalyst volume. The resulting product was found to contain 290 p.p.m. of 2-methylbenzofuran, but no hydroxyacetone. This product can be treated for the removal of the 2-methylbenzofuran by a straight forward extractive distillation step in the presence of water, for instance by refluxing the phenol through a 40-plate Oldershaw column with 20% by weight of water for about 20 hours, followed by dehydration and distillation.

EXAMPLE 2.

A spectroscopically pure sample of cumene hydroperoxide was decomposed by adding it to the product of its own cleavage containing 0.4% concentrated sulphuric acid at 85° C. The final product was neutralised with aqueous sodium carbonate and distilled to give a lower fraction comprising acetone, water and a fraction comprising crude phenol. The crude phenol contained 0.365% hydroxyacetone.

A sample of the phenol fraction was refluxed for 10 minutes over 5% of its weight of a Fullers' Earth (Grade 237 SW marketed

by The Fullers' Earth Union Limited) and filtered free of the earth.

- 5 The Fullers' Earth treated product contained 1660 p.p.m. of 2-methyl-benzofuran, which could be removed by extractive distillation in the presence of water as described in Example 1.

EXAMPLE 3.

- 10 A crude concentrate of 75% cumene hydroperoxide, obtained from the oxidation of cumene followed by the removal of the unreacted hydrocarbons by flash distillation, was decomposed as described in Example 1, and the product was distilled to give a crude
15 phenol fraction, containing about 0.36% hydroxy acetone, but less than 1 p.p.m. of 2-methyl-benzofuran.

- 20 After standing for several months in metal containers the phenol fraction was found to contain about 300 p.p.m. of 2-methyl-benzofuran. This phenol was treated by passing over a Fullers' Earth (Grade 3H2, marketed by The Fullers' Earth Union Limited) in the vapour phase at 190—194° C. The product
25 contained over 1000 p.p.m. of 2-methyl-benzofuran, which could then be removed by extractive distillation in the presence of water as described in Example 1.

EXAMPLE 4.

- 30 A sample of phenol obtained by the oxidation of cumene and the decomposition of the resulting hydroperoxide, was extractively distilled in the presence of water, dehydrated and distilled to give a product which had an intense red colour on sulphonation (absorbing

at 5040 Å) which was not due to the presence of either hydroxyacetone (5140 Å) or 2-methyl-benzofuran (4860 Å).

A sample of this phenol was treated by a process for converting hydroxyacetone into 2-methyl-benzofuran, by vapour phase heat-treatment over a Fullers' Earth catalyst (Grade 249 SW, Fullers' Earth Union Limited) at 192—194° and was subsequently subjected to extractive distillation in the presence of water followed by fractionation. On sulphonation of the resulting phenol, the product had a colour which was ten times less intense than the original sulphonation colour, and was no longer objectionable.

In contrast with the above examples the following experiment illustrates the difficulty of purifying phenol contaminated in this way by straight forward distillation methods.

A sample of phenol derived from the oxidation of cumene and the decomposition of the resulting hydroperoxide, was subjected to extractive distillation in the presence of water followed by fractionation, and was found to contain 0.02% of hydroxyacetone and 70 p.p.m. of 2-methyl-benzofuran. This sample was subjected to a further purification by extractive distillation in the presence of water followed by fractional distillation. The distilled phenol still contained 10 p.p.m. of 2-methyl-benzofuran. After storing at 60° C. in a mild steel vessel in the presence of 0.01% of phosphoric acid for 1 month, the amount of 2-methyl-benzofuran had increased to 90 p.p.m.

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